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Some remarks on cooling curves as a principle tool for solidification characterization

Reza Ghomashchi[a,*], Shahrooz Nafisi[b]

[a] School of Mechanical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia
[b] University of Alberta, AB, Canada

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ABSTRACT

It is shown that the classical approach in interpreting solidification parameters needs to be revisited. The new approach in analyzing cooling curve entails changes in the classic way of measuring undercooling, nucleation start and end temperatures and recalescence. Most importantly, the classical recalescence is shown to be a growth related phenomenon rather than nucleation at the beginning of solidification.

1. Communication

Investigation of cooling curves (temperature-time plots) is an effective tool for the characterization of solidification behavior of engineering alloys. It provides information on nucleation and growth processes to be utilized to better understand the process of liquid to solid transformation during casting and thus improving the integrity of as-cast engineering components. Therefore, extraction of this information from cooling curves is of practical importance. The aim of this communication is to provide insight into the analysis of cooling curves and to highlight differences in the classical interpretation of cooling curves [e.g. 1–3] with those attainable through application of cooling curve analysis or "thermal analysis" [e.g. 4–6]. It is revealed that measurements of the magnitude of undercooling, nucleation and growth temperatures, generally expressed through classical interpretation of cooling curves, are not true indication of the parameters being measured. It is also shown that recalescence, generally attributed to nucleation at the beginning of solidification according to classical view, is a growth related process. The discussion is presented in the context of A356 Al-Si alloy experiments.

Solidification of metals and alloys starts when an appropriate degrees of undercooling (ΔT) is achieved within the bulk molten metal. It entails the formation of stable solid nuclei of radii $r \geq r^*$(r^* is the critical radius below which the solid particle is not stable and remelts), that are able to grow with time [2]. The nuclei of solid phase in the molten bulk are formed when there is a change in the Gibbs free energy (ΔG) associated with the surface free energy (ΔG_S) due to the creation of the surface of the solid phase in the growth medium and the volume excess free energy (ΔG_V) which is the result of creation of the volume of the nuclei in the medium. The free energy change associated with the formation of spherical nuclei of radius r is given by;

$$\Delta G = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G_v \tag{1}$$

where γ (J m^{-2}) is the interfacial tension between the surface of the nucleus and the undercooled melt surrounding it and ΔG_v (J m^{-3}) is the change in the free energy per unit volume ($\Delta G_v = G_L - G_S$, with G_L and G_S as the free energies per unit volume of the liquid and solid phases, respectively). The volume free energy change is negative, $\Delta G_v < 0$, at temperatures below the melting point T_m and is the driving force for solidification. The two terms on the right-hand side of Eq. (1) depend differently on r such that ΔG passes through a maximum corresponding to the critical radius r^*. Taking$\frac{d(\Delta G)}{dr}=0$, one obtains the critical radius r^* as;

$$r^* = \frac{2\gamma}{\Delta G_v} \tag{2}$$

When the radius r of the nuclei equals or exceeds r^*, the free energy change (ΔG) for the formation of a nucleus decreases with an increase in r and the nucleus is stable and grows to larger dimensions. The volume free energy change ΔG_v is related to undercooling ΔT by (for example, see [2]);

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* Corresponding author.
E-mail address: Reza.ghomashchi@adelaide.edu.au (R. Ghomashchi).

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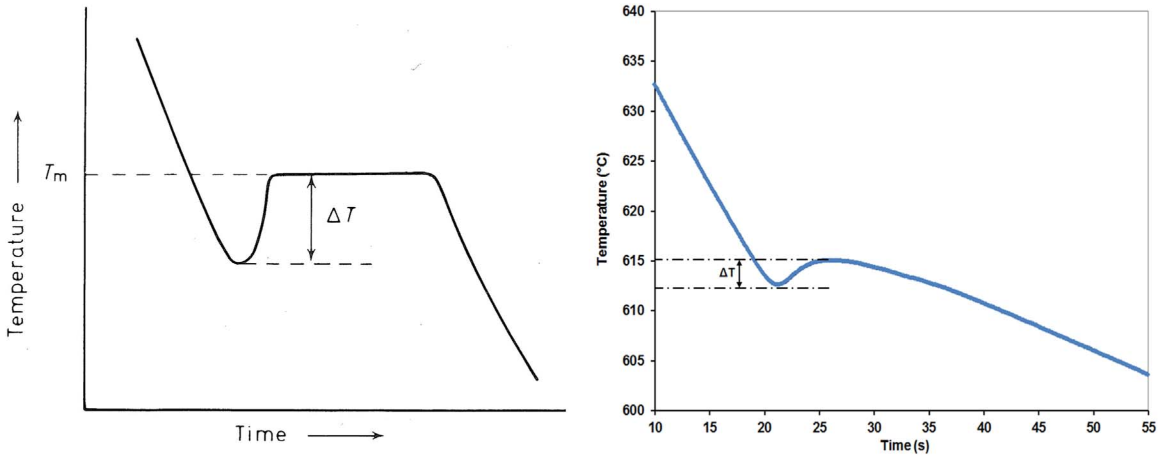

Fig. 1. (a) A sketch showing ΔT in classical approach for pure material [2], (b) actual cooling curve of A356 Al-Si alloy showing ΔT according to the classical approach.

$$\Delta G_v = \frac{\Delta H_f \Delta T}{T_m} \tag{3}$$

Where ΔH_f is the latent heat of fusion (J m^{-3}), ΔT *(the degrees Kelvin or Celsius the melt is cooled below its equilibrium melting point)* is the undercooling (K) and T_m is the melting temperature (K). Substitution of ΔG_v from Eq. (3) into Eq. (2) gives;

$$r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T} \tag{4}$$

According to Eq. (4) the critical radius r^* of a stable nucleus is inversely proportional to the value of undercooling ΔT. The magnitude of undercooling ΔT to initiate nucleation is rather large for homogenous nucleation ($\Delta T \approx 0.2\ T_m$ to $0.3\ T_m$). The undercooling along with other vital information about solidification behavior of alloys is extracted from cooling curves. An example of classical definition of undercooling as well as an actual cooling curve obtained during solidification of A356 Al-Si alloy is shown in Fig. 1 where the undercooling is defined by implementing classical approach.

As illustrated in Fig. 1, in the classical approach of interpreting cooling curves the value of undercooling ΔT is defined as the dip in the recalescence segment. As defined in all textbooks published for undergraduate students [e.g. 1–3], this is the basis of determining undercooling (ΔT), Fig. 1 [2]. However, this is not the case when cooling curves are interpreted using the concept of "thermal analysis (TA)" [4–6], where determination of the critical solidification parameters, such as undercooling, liquidus and solidus temperatures or the formation of various phases during solidification, is based on the first order derivative of cooling curve($\frac{dT}{dt}$), Fig. 2 (first order derivative is an indication of the changes in the energy balance of the system).

On the basis of tremendous work by Backerud et al. [6] and also the work carried out by authors [7], the following critical solidification points are identified on the beginning of the cooling curve for A356 Al-Si alloy as given in Fig. 2:

1. $T_{nuc\text{-}Al}$: Start of primary α-Al dendrites nucleation,
2. $T_{min\text{-}Al}$: Start of the unsteady state growth temperature, the temperature beyond which newly nucleated crystals grow to such extent that the latent heat liberated surpasses the heat extracted from the sample,
3. $T_{g\text{-}Al}$: Start of steady state growth temperature due to release of latent heat of primary α-Al dendrites,
4. ΔT_{Rec}: Recalescence, Temperature difference between unsteady ($T_{min\text{-}Al}$) and the start of steady ($T_{g\text{-}Al}$) states growth temperatures of primary α-Al particles
5. t_{Rec}: Recalescence time, time difference between the times $t_{min\text{-}Al}$ and $t_{g\text{-}Al}$ associated with $T_{min\text{-}Al}$ and $T_{g\text{-}Al}$,

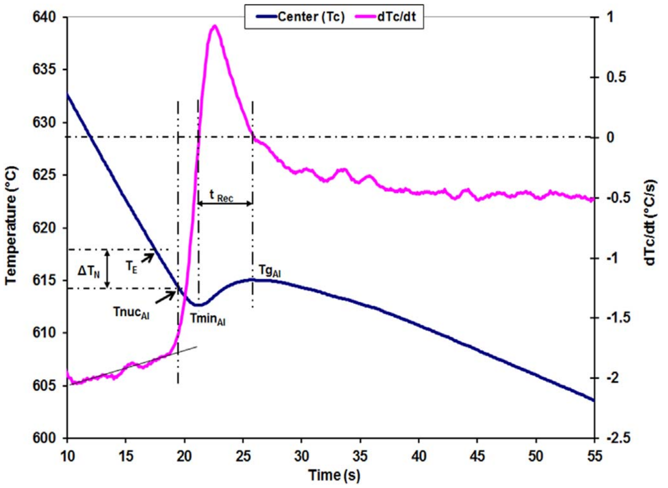

Fig. 2. Cooling curve and first derivative of A356 Al-Si alloy at the commencement of solidification (α-Al primary particles formation).

In most academic textbooks (e.g. see [1–3]) undercooling is defined as the difference between $T_{min\text{-}Al}$ and $T_{g\text{-}Al}$, where $T_{min\text{-}Al}$ is classically believed to be the starting point of the solidification process, nucleation. However, in the thermal analysis methodology, nucleation starts at a temperature ($T_{nuc\text{-}Al}$) slightly higher than that identified in the classic approach; Fig. 2. Backerud et al. [6] defined nucleation undercooling (ΔT_N) as the difference between the equilibrium liquidus temperature (T_E), not discernible from cooling curve, and the start of nucleation ($T_{nuc\text{-}Al}$), $\Delta T_N = T_E - T_{nuc\text{-}Al}$, which is detectable by sudden change in the first order derivative curve. The reason for identifying such a point as the nucleation start point is the change in the slope of the first order derivative of temperature-time graph($\frac{dT}{dt}$), which is an indication of the changes in the energy balance of the system. This change is only due to phase change, formation of solid particles. As nucleation proceeds, the released latent heat due to nuclei formation is dissipated out via heat extraction from the molten pool with cooling continues. However, at point $T_{min\text{-}Al}$, the latent heat released by the nuclei balances out the heat extracted from the mold. It is beyond this point that molten pool temperature increases with time in spite of heat being continuously extracted from the system. The authors believe nucleation is completed (at the tip of thermocouple which the actual measurements are taken) at $T_{min\text{-}Al}$ and the rise in melt temperature beyond this point is due to growth, termed as *"unsteady growth"*. The changes in heat balance of the system beyond this point warrant the formation of sufficiently high solid fraction. This is not feasible by mere nucleating of fine solid particles which are expected to not only